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(54) Title: LOW PRESSURE SEPARATION OF DIMETHYL ETHER FROM AN OLEFIN STREAM

(57) Abstract: Disclosed is a method of removing dimethyl ether from an ethylene and/or propylene containing stream. Dimethyl ether is removed at a low pressure preferably in a distillation column. The low pressure separation has the benefit of providing a relatively low temperature separation, while allowing for recovery of a highly concentrated ethylene and/or propylene stream.

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## LOW PRESSURE SEPARATION OF DIMETHYL ETHER FROM AN OLEFIN STREAM

### Field of the Invention

[0001] This invention is directed to a method of removing oxygenated contaminants from an olefin stream. In particular, this invention is directed to a method of removing dimethyl ether from an ethylene and/or propylene containing stream.

### Background of the Invention

[0002] Olefins, particularly C<sub>2</sub> and C<sub>3</sub> olefins, are desirable as a feed source for making derivative products such as oligomers, e.g., higher olefins, and polymers such as polyethylene and polypropylene. Olefin feed sources have traditionally been produced by cracking petroleum feedstocks.

[0003] U.S. Patent No. 5,090,977 discloses a method of making olefins by steam cracking. The method includes separating the olefin product into methane, hydrogen, ethane, ethylene, propylene and C<sub>5</sub>+ streams. The disclosed separation preferentially produces propylene, and no propane, butane, butene, or butadiene streams are produced.

[0004] Oxygenate feed stocks, however, are becoming an alternative to petroleum feed stocks for making olefins, particularly large quantities of ethylene and propylene for the production of higher olefins and plastic materials. In general, the olefins are formed by contacting the oxygenate components with a molecular sieve catalyst to catalytically convert the oxygenates to olefins.

[0005] For example, U.S. Patent No. 4,499,327, discloses a process for making olefins from methanol using any of a variety of silicoaluminophosphate (SAPO) molecular sieve catalysts. The process is carried out at a temperature between 300°C and 500°C, a pressure between 0.1 atmosphere to 100 atmospheres, and a weight hourly space velocity (WHSV) of between 0.1 and 40 hr<sup>-1</sup>. The process is highly selective for making ethylene and propylene.

[0006] U.S. Patent No. 6,121,504 also discloses a method of making olefin product from oxygenate feed using molecular sieve catalysts. Water and other

unwanted by-products are removed from the olefin product by contacting with a quench medium. After contacting with the quench medium, a light product fraction is obtained which comprises the desired olefins, but also includes dimethyl ether, methane, CO, CO<sub>2</sub>, ethane, propane, and other minor components such as water and unreacted oxygenate feedstock.

[0007] In order to further process olefins, it is often necessary to reduce or remove undesirable by-products that are present in the olefin composition. For example, U.S. Patent No. 4,474,647 discloses that dimethyl ether can adversely impact the oligomerization of certain olefins. The patent describes a process for removing dimethyl ether from a C<sub>4</sub> and/or C<sub>5</sub> olefin stream using distillation. The stream is distilled and separated into an overhead and a bottoms stream. The overhead stream contains dimethyl ether, water, and various hydrocarbons, and the bottoms stream contains purified olefins.

[0008] U.S. Patent No. 5,914,433 discloses a method of making an olefin composition, and a system for removing non-olefin by-products such as CO<sub>2</sub>. A dewatered olefin composition is washed with caustic to remove CO<sub>2</sub>, and the washed olefin composition is dried to reduce water added as a result of the caustic wash.

[0009] U.S. Patent No. 5,720,929 discloses a process which includes making isobutylene from isobutane. The isobutylene is cooled and water is stripped from the product. Additional water is removed by washing the product with methanol.

[0010] Eng et al., "Integration of the UOP/HYDRO MTO Process into Ethylene Plants," 10th Ethylene Producers' Conference, 1998, disclose a flow scheme for making an olefin composition from methanol. The flow scheme shows that methanol and dimethyl ether are compressed out of the olefin product and recycled back to the methanol to the olefin reactor, with ethylene and propylene being recovered.

[0011] EP-B1-0 060 103 discloses a process for extracting dimethyl ether from a vapor stream containing ethylene and propylene using a methanol wash system. The methanol wash removes a substantial amount of the dimethyl ether, but also removes a significant amount of the ethylene and propylene.

[0012] Additional methods of removing undesirable components from olefin streams are sought. In particular, methods for removing oxygenated hydrocarbons, particularly dimethyl ether, as well as CO<sub>2</sub> and water down to the ppm level in olefin product streams, and without removing significant amounts of olefin, are sought.

#### Summary of the Invention

[0013] In this invention, dimethyl ether is separated from an olefin stream containing ethylene and/or propylene using low pressure separation, preferably low pressure distillation. In one embodiment, the invention provides a method of separating dimethyl ether from an olefin stream which comprises providing an olefin stream containing ethylene, ethane, propylene, propane, and dimethyl ether. The provided stream is separated into a first fraction and a second fraction at a pressure of less than 200 psig. The first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream. In another embodiment, the provided olefin stream further contains water in an amount not greater than about 15,000 wppm.

[0014] The invention is particularly effective on olefin streams which contain at least about 500 wppm dimethyl ether. Preferably, the olefin stream contains not greater than about 50 wt % dimethyl ether.

[0015] In one embodiment, the separation is such that the first fraction contains at least a majority of the propane present in the olefin stream, and preferably not greater than about 100 wppm dimethyl ether. The separation can be such that a majority of the propane present in the olefin stream can be either in the first or second fraction. The separation can also be such that a majority of propadiene, which can also be present in the olefin stream, can be either in the first or second fraction. To obtain very high purity propylene streams from the olefin stream, it is preferred that a majority of any propadiene and propane present in the olefin feed be separated out in the second fraction.

[0016] In another embodiment, the olefin stream is separated into the first fraction and the second fraction in a distillation column. Preferably, water absorbent is added to the distillation column. Water absorbent can be added to the distillation column at a molar ratio of water absorbent to total olefin stream to be separated of from about 4:1 to about 1:5,000.

[0017] In yet another embodiment of the invention, the first fraction is acid gas treated. The acid gas treated stream can subsequently be water washed and contacted with solid adsorbent material.

[0018] The ethylene and propylene separated from the olefin stream can be used in any ethylene or propylene derivative process, due to the high quality of the recovered streams. Preferred embodiments include polymerization into polyethylene and polypropylene.

[0019] In another embodiment, the invention provides a method of separating dimethyl ether from an olefin stream which comprises contacting oxygenate with a molecular sieve catalyst to form an olefin stream, wherein the olefin stream contains ethylene, ethane, propylene, propane, and dimethyl ether. The olefin stream is separated into a first fraction and a second fraction at a pressure of less than 1380 kPa (200 psig). The first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream.

[0020] In one embodiment of the invention, the olefin stream formed from contacting the oxygenate with the molecular sieve catalyst is contacted with water absorbent prior to separating into the first and second fraction. It is desired that the water absorbent be contacted with the olefin stream at a molar ratio of water absorbent to total olefin of about 1:2 to about 1:200. Preferably, the olefin stream contacted with the water absorbent contains water in an amount not greater than about 15,000 wppm.

[0021] The invention further provides a method of separating dimethyl ether from an olefin stream which comprises contacting oxygenate with a molecular sieve catalyst to form an olefin stream, wherein the olefin stream contains

ethylene, ethane, propylene, propane, dimethyl ether and water. The water is then removed from the olefin stream so that the olefin stream contains not greater than about 15,000 wppm water. The olefin stream containing not greater than about 15,000 wppm water is then separated into a first fraction and a second fraction at a pressure of less than 1380 kPa (200 psig), wherein the first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream.

[0022] There is further provided in this invention a method of separating dimethyl ether from an olefin stream which comprises providing an olefin stream containing ethylene, ethane, propylene, propane, propadiene and dimethyl ether. The olefin stream is separated into a first fraction containing at least a majority of the ethylene and propylene present in the olefin stream, and a second fraction containing at least a majority of the dimethyl ether and propadiene present in the olefin stream. Separation is performed at a pressure of less than 1380 kPa (200 psig) and such that the second fraction has an average temperature of not greater than about 99°C (210°F).

[0023] In another embodiment of the invention, there is provided a method of separating dimethyl ether from an olefin stream which comprises providing an olefin stream containing ethylene, ethane, propylene, propane, and dimethyl ether. In this embodiment, the olefin stream is separated into a first fraction and a second fraction in a distillation column, with the first fraction containing at least a majority of the ethylene and propylene present in the olefin stream. The second fraction contains at least a majority of the dimethyl ether present in the olefin stream. Preferably, the provided olefin stream contains not greater than about 15,000 wppm water, and the second fraction has an average temperature of not greater than about 99°C (210°F).

#### Brief Description of the Drawings

[0024] Various embodiments of the overall invention are shown by way of example in the attached Figures, wherein:

Fig. 1 is a flow diagram showing a process for reacting methanol to form an olefin, with the olefin being separated into a first fraction containing ethylene and propylene and a second fraction containing dimethyl ether and  $C_4+$  hydrocarbon components; and

Fig. 2 is a flow diagram showing treatment of ethylene and propylene by caustic wash, water wash, and adsorption.

#### Detailed Description of the Invention

[0025] This invention provides a method for removing oxygenated hydrocarbon components such as dimethyl ether from an olefin stream. It is *desirable to remove such components*, since they may poison catalysts that are used to further process olefins in the olefin stream. The invention is particularly beneficial for removing dimethyl ether from an ethylene and/or propylene stream so that the ethylene and/or propylene can be polymerized without poisoning catalyst used in the polymerization reaction.

[0026] In this invention, oxygenated contaminants, particularly including dimethyl ether, are removed from the provided olefin stream at low pressure. An advantage of using a low pressure separation is that lower temperatures can be obtained in the heavier fractions separated during the separation process. A benefit of lower temperatures is that there will be fewer equipment fouling problems. In addition, such a process will use a lower energy input to run associated operating equipment such as reboilers and condensers.

[0027] Another advantage in low pressure separation is that less energy will be required to maintain system separation pressure. This means that compressors having fewer stages can be more readily utilized.

[0028] In general, the method of this invention comprises providing an olefin stream which contains ethylene, ethane, propylene, propane, and dimethyl ether, then separating at least a majority, i.e., greater than 50%, of the dimethyl ether present in the olefin stream. The olefin stream can come from any conventional source. However, this invention is particularly effective in

separating dimethyl ether from olefin streams made from an oxygenate to olefin process.

[0029] In one embodiment, the olefin stream that is provided comprises not greater than about 50 wt % dimethyl ether, preferably not greater than about 20 wt % dimethyl ether, more preferably not greater than about 10 wt % dimethyl ether, and most preferably not greater than about 5 wt % dimethyl ether. Of course, for dimethyl ether to be removed from the olefin stream, some measurable amount must be present. Desirably, the provided olefins stream will contain at least about 100 wppm dimethyl ether, preferably at least about 500 wppm dimethyl ether, and more preferably at least about 1,000 wppm dimethyl ether.

[0030] In another embodiment, the olefin stream that is provided comprises at least about 25 wt % ethylene. Preferably, the provided olefin stream comprises from about 25 wt % ethylene to about 75 wt % ethylene, more preferably from about 30 wt % to about 60 wt %, and most preferably from about 35 wt % to about 50 wt % propylene.

[0031] In another embodiment, the olefin stream that is provided also comprises at least about 20 wt % propylene. Preferably, the provided olefin stream comprises from about 20 wt % propylene to about 70 wt % propylene, more preferably from about 25 wt % to about 50 wt % propylene, and most preferably from about 30 wt % to about 40 wt % propylene.

[0032] It is desirable that the provided olefin stream contain a relatively low concentration of ethane, preferably a lower concentration of ethane than propane. Preferably, the olefin stream comprises not greater than about 4 wt % ethane, more preferably not greater than about 3 wt % ethane, and most preferably not greater than about 2 wt % ethane.

[0033] It is also desirable that the provided olefin stream contain a relatively low concentration of propane. Preferably, the olefin stream comprises not greater than about 5 wt % propane, more preferably not greater than about 4 wt % propane, and most preferably not greater than about 3 wt % propane.

[0034] In another embodiment of the invention, the provided olefin stream contains both ethylene and propylene. Desirably, the olefin stream contains at



least about 50 wt % ethylene and propylene. Preferably, the olefin stream contains from about 50 wt % to about 95 wt % ethylene and propylene, more preferably from about 55 wt % to about 90 wt % ethylene and propylene, and most preferably from about 60 wt % to about 85 wt % ethylene and propylene.

[0035] The provided olefin stream can also contain some amount of water. However, it is desirable that any water present in the olefin stream will be at a concentration such that free water formation (i.e., formation of a separate water phase) or gas hydration does not significantly impede the separation process. Gas hydration results in the formation of clathrate compounds. Such compounds are solids, and these solids can cause significant operational problems in the separation process.

[0036] Water that is present in the provided olefin stream should be at a concentration sufficiently low such that a separate water phase is not formed during the separation process. This is particularly important when a distillation column having trays is used to separate the dimethyl ether from the olefin, since a separate water phase formed in the trays will impede mass transfer. Distillation columns having packing are preferred at higher concentrations of water, since such columns will not be prone to collect separate water phases.

[0037] It is desirable in this invention that the provided olefin stream contain not greater than about 15,000 wppm water. Preferably the olefin stream contains not greater than about 10,000 wppm water, more preferably not greater than 5,000 wppm water, and most preferably not greater than about 1,000 wppm water.

[0038] It is not necessary in this invention that the olefin stream be completely dry. That is, the olefin stream can contain some water. The benefit of the olefin stream containing some amount of water is that additional and/or complex drying equipment will not be needed before separating the dimethyl ether from the olefin stream. Preferably, the olefin stream contains at least about 10 wppm water, more preferably at least about 20 wppm water, and most preferably at least about 25 wppm water.

[0039] If an olefin stream contains an unacceptably high concentration of water, a sufficient amount of the water can be removed either prior to or during

separation of the dimethyl ether using a water absorbent. Examples of water absorbents include alcohols, amines, amides, nitriles, heterocyclic nitrogen containing compounds, or a combination of any of the preceding. Either monohydric alcohols or polyhydric alcohols can be used as the alcohol absorbent. Specific examples of absorbents include methanol, ethanol, propanol, ethylene glycol, diethylene glycol, triethylene glycol, ethanolamine, diethanolamine, triethanolamine, hindered cyclic amines, acetonitrile, n-methylpyrrolidone, dimethyl formamide, and combinations thereof.

**[0040]** To obtain a substantial degree of effectiveness, the water absorbent should contain little non-water absorbing components. For example, the water absorbent should contain at least about 75 wt % water absorbing components. Desirably, the water absorbent contains at least about 90 wt %, preferably at least about 95 wt %, and most preferably at least about 98 wt % water absorbent.

**[0041]** When a water absorbent is used to reduce the concentration of water in the olefin stream prior to separation of the dimethyl ether, a wash type of process using a wash vessel can be used. In essence, a wash process is one in which the olefin stream is contacted with water absorbent such that a substantial amount of the water is removed, i.e., washed out, from the olefin stream. The amount of absorbent added to the wash vessel should be sufficient to substantially reduce free water formation (i.e., formation of a separate liquid phase), particularly in the vessel in which the separation of the dimethyl ether from the olefin takes place. In this embodiment, it is desirable that water absorbent be added to the wash vessel at a mole ratio of absorbent compound to total olefin feed to the wash vessel of about 1:2 to about 1:200. Preferably, the absorbent is added at a mole ratio of from about 1:5 to about 1:100, and more preferably from about 1:10 to about 1:50.

**[0042]** Although the olefin stream can come from any conventional source which contains dimethyl ether, the invention is particularly suited to removing dimethyl ether from olefin streams made from an oxygenate to olefin process. In one embodiment of this invention, an olefin stream containing dimethyl ether is obtained by contacting oxygenate feedstock with a molecular sieve catalyst.

**[0043]** In a preferred embodiment of the process of the invention, the oxygenate feedstock contains one or more oxygenates, more specifically, one or more organic compound(s) containing at least one oxygen atom. In the most preferred embodiment of the process of invention, the oxygenate in the feedstock is one or more alcohol(s), preferably aliphatic alcohol(s) where the aliphatic moiety of the alcohol(s) has from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, and most preferably from 1 to 4 carbon atoms. The alcohols useful as feedstock in the process of the invention include lower straight and branched chain aliphatic alcohols and their unsaturated counterparts. Non-limiting examples of oxygenates include methanol, ethanol, n-propanol, isopropanol, methyl ethyl ether, dimethyl ether, diethyl ether, di-isopropyl ether, formaldehyde, dimethyl carbonate, dimethyl ketone, acetic acid, and mixtures thereof. In the most preferred embodiment, the feedstock is selected from one or more of methanol, ethanol, dimethyl ether, diethyl ether or a combination thereof, more preferably methanol and dimethyl ether, and most preferably methanol.

**[0044]** The feedstock, in one embodiment, contains one or more diluent(s), typically used to reduce the concentration of the feedstock, and are generally non-reactive to the feedstock or molecular sieve catalyst composition. Non-limiting examples of diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water, essentially non-reactive paraffins (especially alkanes such as methane, ethane, and propane), essentially non-reactive aromatic compounds, and mixtures thereof. The most preferred diluents are water and nitrogen, with water being particularly preferred.

**[0045]** The diluent is either added directly to a feedstock entering into a reactor or added directly into a reactor, or added with a molecular sieve catalyst composition. In one embodiment, the amount of diluent in the feedstock is in the range of from about 1 to about 99 mole percent based on the total number of moles of the feedstock and diluent, preferably from about 1 to 80 mole percent, more preferably from about 5 to about 50, most preferably from about 5 to about 25. In one embodiment, other hydrocarbons are added to a feedstock either directly or indirectly, and include olefin(s), paraffin(s), aromatic(s) (see for

example U.S. Patent No. 4,677,242, addition of aromatics) or mixtures thereof, preferably propylene, butylene, pentylene, and other hydrocarbons having 4 or more carbon atoms, or mixtures thereof.

**[0046]** Molecular sieves capable of converting an oxygenate to an olefin compound include zeolite as well as non-zeolite molecular sieves, and are of the large, medium or small pore type. Non-limiting examples of these molecular sieves are the small pore molecular sieves, AEI, AFT, APC, ATN, ATT, ATV, AWW, BIK, CAS, CHA, CHI, DAC, DDR, EDI, ERI, GOO, KFI, LEV, LOV, LTA, MON, PAU, PHI, RHO, ROG, THO, and substituted forms thereof; the medium pore molecular sieves, AFO, AEL, EUO, HEU, FER, MEL, MFI, MTW, MTT, TON, and substituted forms thereof; and the large pore molecular sieves, EMT, FAU, and substituted forms thereof. Other molecular sieves include ANA, BEA, CFI, CLO, DON, GIS, LTL, MER, MOR, MWW and SOD. Non-limiting examples of the preferred molecular sieves, particularly for converting an oxygenate containing feedstock into olefin(s), include AEL, AFY, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TAM and TON. In one preferred embodiment, the molecular sieve of the invention has an AEI topology or a CHA topology, or a combination thereof, most preferably a CHA topology.

**[0047]** Molecular sieve materials all have 3-dimensional, four-connected framework structure of corner-sharing  $\text{TO}_4$  tetrahedra, where T is any tetrahedrally coordinated cation. These molecular sieves are typically described in terms of the size of the ring that defines a pore, where the size is based on the number of T atoms in the ring. Other framework-type characteristics include the arrangement of rings that form a cage, and when present, the dimension of channels, and the spaces between the cages. See van Bekkum, et al., *Introduction to Zeolite Science and Practice, Second Completely Revised and Expanded Edition*, Volume 137, pages 1-67, Elsevier Science, B.V., Amsterdam, Netherlands (2001).

**[0048]** The small, medium and large pore molecular sieves have from a 4-ring to a 12-ring or greater framework-type. In a preferred embodiment, the

molecular sieves have 8-, 10- or 12- ring structures or larger and an average pore size in the range of from about 3 Å to 15 Å. In the most preferred embodiment, the molecular sieves of the invention, preferably silicoaluminophosphate molecular sieves, have 8- rings and an average pore size less than about 5 Å, preferably in the range of from 3 Å to about 5 Å, more preferably from 3 Å to about 4.5 Å, and most preferably from 3.5 Å to about 4.2 Å.

**[0049]** Molecular sieves, particularly zeolitic and zeolitic-type molecular sieves, preferably have a molecular framework of one, preferably two or more corner-sharing  $[TO_4]$  tetrahedral units, more preferably, two or more  $[SiO_4]$ ,  $[AlO_4]$  and/or  $[PO_4]$  tetrahedral units, and most preferably  $[SiO_4]$ ,  $[AlO_4]$  and  $[PO_4]$  tetrahedral units. These silicon, aluminum, and phosphorous based molecular sieves and metal containing silicon, aluminum and phosphorous based molecular sieves have been described in detail in numerous publications including for example, U.S. Patent No. 4,567,029 (MeAPO where Me is Mg, Mn, Zn, or Co), U.S. Patent No. 4,440,871 (SAPO), European Patent Application EP-A-0 159 624 (ELAPSO where El is As, Be, B, Cr, Co, Ga, Ge, Fe, Li, Mg, Mn, Ti or Zn), U.S. Patent No. 4,554,143 (FeAPO), U.S. Patents No. 4,822,478, 4,683,217, 4,744,885 (FeAPSO), EP-A-0 158 975 and U.S. Patent No. 4,935,216 (ZnAPSO, EP-A-0 161 489 (CoAPSO), EP-A-0 158 976 (ELAPO, where EL is Co, Fe, Mg, Mn, Ti or Zn), U.S. Patent No. 4,310,440 ( $AlPO_4$ ), EP-A-0 158 350 (SENAPSO), U.S. Patent No. 4,973,460 (LiAPSO), U.S. Patent No. 4,789,535 (LiAPO), U.S. Patent No. 4,992,250 (GeAPSO), U.S. Patent No. 4,888,167 (GeAPO), U.S. Patent No. 5,057,295 (BAPSO), U.S. Patent No. 4,738,837 (CrAPSO), U.S. Patents Nos. 4,759,919, and 4,851,106 (CrAPO), U.S. Patents Nos. 4,758,419, 4,882,038, 5,434,326 and 5,478,787 (MgAPSO), U.S. Patent No. 4,554,143 (FeAPO), U.S. Patent No. 4,894,213 (AsAPSO), U.S. Patent No. 4,913,888 (AsAPO), U.S. Patents Nos. 4,686,092, 4,846,956 and 4,793,833 (MnAPSO), U.S. Patents Nos. 5,345,011 and 6,156,931 (MnAPO), U.S. Patent No. 4,737,353 (BeAPSO), U.S. Patent No. 4,940,570 (BeAPO), U.S. Patents Nos. 4,801,309, 4,684,617 and 4,880,520 (TiAPSO), U.S. Patents Nos. 4,500,651, 4,551,236 and 4,605,492 (TiAPO), U.S. Patents No. 4,824,554, 4,744,970 (CoAPSO), U.S.

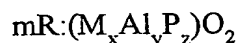
Patent No. 4,735,806 (GaAPSO) EP-A-0 293 937 (QAPSO, where Q is framework oxide unit  $[QO_2]$ ), as well as U.S. Patents Nos. 4,567,029, 4,686,093, 4,781,814, 4,793,984, 4,801,364, 4,853,197, 4,917,876, 4,952,384, 4,956,164, 4,956,165, 4,973,785, 5,241,093, 5,493,066 and 5,675,050, all of which are herein fully incorporated by reference.

**[0050]** Other molecular sieves include those described in EP-0 888 187 B1 (microporous crystalline metallophosphates,  $SAPO_4$  (UIO-6)), U.S. Patent No. 6,004,898 (molecular sieve and an alkaline earth metal), U.S. Patent Application Serial No. 09/511,943 filed February 24, 2000 (integrated hydrocarbon co-catalyst), PCT WO 01/64340 published September 7, 2001 (thorium containing molecular sieve), and R. Szostak, *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, New York (1992), which are all herein fully incorporated by reference.

**[0051]** The more preferred silicon, aluminum and/or phosphorous containing molecular sieves, and aluminum, phosphorous, and optionally silicon, containing molecular sieves include aluminophosphate (ALPO) molecular sieves and silicoaluminophosphate (SAPO) molecular sieves and substituted, preferably metal substituted, ALPO and SAPO molecular sieves. The most preferred molecular sieves are SAPO molecular sieves, and metal substituted SAPO molecular sieves. In an embodiment, the metal is an alkali metal of Group IA of the Periodic Table of Elements, an alkaline earth metal of Group IIA of the Periodic Table of Elements, a rare earth metal of Group IIIB, including the Lanthanides: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium; and scandium or yttrium of the Periodic Table of Elements, a transition metal of Groups IVB, VB, VIB, VIIB, VIIIB, and IB of the Periodic Table of Elements, or mixtures of any of these metal species. In one preferred embodiment, the metal is selected from the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr, and mixtures thereof. In another preferred embodiment, these metal atoms discussed above are inserted into the framework of a molecular sieve through a tetrahedral unit, such as  $[MeO_2]$ , and carry a net

charge depending on the valence state of the metal substituent. For example, in one embodiment, when the metal substituent has a valence state of +2, +3, +4, +5, or +6, the net charge of the tetrahedral unit is between -2 and +2.

**[0052]** In one embodiment, the molecular sieve, as described in many of the U.S. Patents mentioned above, is represented by the empirical formula, on an anhydrous basis:



wherein R represents at least one templating agent, preferably an organic templating agent; m is the number of moles of R per mole of  $(M_xAl_yP_z)O_2$  and m has a value from 0 to 1, preferably 0 to 0.5, and most preferably from 0 to 0.3; x, y, and z represent the mole fraction of Al, P and M as tetrahedral oxides, where M is a metal selected from one of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIB, VIIIB and Lanthanide's of the Periodic Table of Elements, preferably M is selected from one of the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr. In an embodiment, m is greater than or equal to 0.2, and x, y and z are greater than or equal to 0.01.

**[0053]** In another embodiment, m is greater than 0.1 to about 1, x is greater than 0 to about 0.25, y is in the range of from 0.4 to 0.5, and z is in the range of from 0.25 to 0.5, more preferably m is from 0.15 to 0.7, x is from 0.01 to 0.2, y is from 0.4 to 0.5, and z is from 0.3 to 0.5.

**[0054]** Non-limiting examples of SAPO and ALPO molecular sieves used in the invention include one or a combination of SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44 (U.S. Patent No. 6,162,415), SAPO-47, SAPO-56, ALPO-5, ALPO-11, ALPO-18, ALPO-31, ALPO-34, ALPO-36, ALPO-37, ALPO-46, and metal containing molecular sieves thereof. The more preferred zeolite-type molecular sieves include one or a combination of SAPO-18, SAPO-34, SAPO-35, SAPO-44, SAPO-56, ALPO-18 and ALPO-34, even more preferably one or a combination of SAPO-18, SAPO-34, ALPO-34 and ALPO-18, and metal containing molecular sieves thereof, and

most preferably one or a combination of SAPO-34 and ALPO-18, and metal containing molecular sieves thereof.

[0055] In an embodiment, the molecular sieve is an intergrowth material having two or more distinct phases of crystalline structures within one molecular sieve composition. In particular, intergrowth molecular sieves are described in the U.S. Patent Application Serial No. 09/924,016 filed August 7, 2001 and PCT WO 98/15496 published April 16, 1998, both of which are herein fully incorporated by reference. In another embodiment, the molecular sieve comprises at least one intergrown phase of AEI and CHA framework-types. For example, SAPO-18, ALPO-18 and RUW-18 have an AEI framework-type, and SAPO-34 has a CHA framework-type.

[0056] In one embodiment, the molecular sieves used in the invention are combined with one or more other molecular sieves. In another embodiment, the preferred silicoaluminophosphate or aluminophosphate molecular sieves, or a combination thereof, are combined with one more of the following non-limiting examples of molecular sieves described in the following: Beta (U.S. Patent No. 3,308,069), ZSM-5 (U.S. Patent Nos. 3,702,886, 4,797,267 and 5,783,321), ZSM-11 (U.S. Patent No. 3,709,979), ZSM-12 (U.S. Patent No. 3,832,449), ZSM-12 and ZSM-38 (U.S. Patent No. 3,948,758), ZSM-22 (U.S. Patent No. 5,336,478), ZSM-23 (U.S. Patent No. 4,076,842), ZSM-34 (U.S. Patent No. 4,086,186), ZSM-35 (U.S. Patent No. 4,016,245), ZSM-48 (U.S. Patent No. 4,397,827), ZSM-58 (U.S. Patent No. 4,698,217), MCM-1 (U.S. Patent No. 4,639,358), MCM-2 (U.S. Patent No. 4,673,559), MCM-3 (U.S. Patent No. 4,632,811), MCM-4 (U.S. Patent No. 4,664,897), MCM-5 (U.S. Patent No. 4,639,357), MCM-9 (U.S. Patent No. 4,880,611), MCM-10 (U.S. Patent No. 4,623,527), MCM-14 (U.S. Patent No. 4,619,818), MCM-22 (U.S. Patent No. 4,954,325), MCM-41 (U.S. Patent No. 5,098,684), M-41S (U.S. Patent No. 5,102,643), MCM-48 (U.S. Patent No. 5,198,203), MCM-49 (U.S. Patent No. 5,236,575), MCM-56 (U.S. Patent No. 5,362,697), ALPO-11 (U.S. Patent No. 4,310,440), titanium aluminosilicates (TASO), TASO-45 (EP-A- 0 229,- 295), boron silicates (U.S. Patent No. 4,254,297), titanium aluminophosphates (TAPO) (U.S. Patent No. 4,500,651),



mixtures of ZSM-5 and ZSM-11 (U.S. Patent No. 4,229,424), ECR-18 (U.S. Patent No. 5,278,345), SAPO-34 bound ALPO-5 (U.S. Patent No. 5,972,203), PCT WO 98/57743 published December 23, 1988 (molecular sieve and Fischer-Tropsch), U.S. Patent No. 6,300,535 (MFI-bound zeolites), and mesoporous molecular sieves (U.S. Patent Nos. 6,284,696, 5,098,684, 5,102,643 and 5,108,725), which are all herein fully incorporated by reference.

**[0057]** The molecular sieves are made or formulated into catalysts by combining the synthesized molecular sieves with a binder and/or a matrix material to form a molecular sieve catalyst composition or a formulated molecular sieve catalyst composition. This formulated molecular sieve catalyst composition is formed into useful shape and sized particles by conventional techniques such as spray drying, pelletizing, extrusion, and the like.

**[0058]** There are many different binders that are useful in forming the molecular sieve catalyst composition. Non-limiting examples of binders that are useful alone or in combination include various types of hydrated alumina, silicas, and/or other inorganic oxide sol. One preferred alumina containing sol is aluminum chlorhydrol. The inorganic oxide sol acts like glue binding the synthesized molecular sieves and other materials such as the matrix together, particularly after thermal treatment. Upon heating, the inorganic oxide sol, preferably having a low viscosity, is converted into an inorganic oxide matrix component. For example, an alumina sol will convert to an aluminum oxide matrix following heat treatment.

**[0059]** Aluminum chlorhydrol, a hydroxylated aluminum based sol containing a chloride counter ion, has the general formula of  $Al_mO_n(OH)_oCl_p \cdot x(H_2O)$  wherein m is 1 to 20, n is 1 to 8, o is 5 to 40, p is 2 to 15, and x is 0 to 30. In one embodiment, the binder is  $Al_{13}O_4(OH)_{24}Cl_7 \cdot 12(H_2O)$  as is described in G.M. Wolterman, et al., Stud. Surf. Sci. and Catal., 76, pages 105-144 (1993), which is herein incorporated by reference. In another embodiment, one or more binders are combined with one or more other non-limiting examples of alumina materials such as aluminum oxyhydroxide,  $\gamma$ -alumina, boehmite, diaspor, and transitional aluminas such as  $\alpha$ -alumina,  $\beta$ -alumina,  $\gamma$ -alumina,  $\delta$ -

alumina,  $\epsilon$ -alumina,  $\kappa$ -alumina, and  $\rho$ -alumina, aluminum trihydroxide, such as gibbsite, bayerite, nordstrandite, doyleite, and mixtures thereof.

[0060] In another embodiment, the binders are alumina sols, predominantly comprising aluminum oxide, optionally including some silicon. In yet another embodiment, the binders are peptized alumina made by treating alumina hydrates such as pseudoboehmite, with an acid, preferably an acid that does not contain a halogen, to prepare sols or aluminum ion solutions. Non-limiting examples of commercially available colloidal alumina sols include Nalco 8676 available from Nalco Chemical Co., Naperville, Illinois, and Nyacol available from The PQ Corporation, Valley Forge, Pennsylvania.

[0061] The molecular sieve, in a preferred embodiment, is combined with one or more matrix material(s). Matrix materials are typically effective in reducing overall catalyst cost, act as thermal sinks assisting in shielding heat from the catalyst composition for example during regeneration, densifying the catalyst composition, increasing catalyst strength such as crush strength and attrition resistance, and to control the rate of conversion in a particular process.

[0062] Non-limiting examples of matrix materials include one or more of: rare earth metals, metal oxides including titania, zirconia, magnesia, thoria, beryllia, quartz, silica or sols, and mixtures thereof, for example silica-magnesia, silica-zirconia, silica-titania, silica-alumina and silica-alumina-thoria. In an embodiment, matrix materials are natural clays such as those from the families of montmorillonite and kaolin. These natural clays include sabbentonites and those kaolins known as, for example, Dixie, McNamee, Georgia and Florida clays. Non-limiting examples of other matrix materials include: halloysite, kaolinite, dickite, nacrite, or anauxite. In one embodiment, the matrix material, preferably any of the clays, are subjected to well known modification processes such as calcination and/or acid treatment and/or chemical treatment.

[0063] In one preferred embodiment, the matrix material is a clay or a clay-type composition, preferably the clay or clay-type composition having a low iron or titania content, and most preferably the matrix material is kaolin. Kaolin has been found to form a pumpable, high solid content slurry, it has a low fresh

surface area, and it packs together easily due to its platelet structure. A preferred average particle size of the matrix material, most preferably kaolin, is from about 0.1  $\mu\text{m}$  to about 0.6  $\mu\text{m}$  with a D90 particle size distribution of less than about 1  $\mu\text{m}$ .

[0064] In another embodiment, the weight ratio of the binder to the matrix material used in the formation of the molecular sieve catalyst composition is from 0:1 to 1:15, preferably 1:15 to 1:5, more preferably 1:10 to 1:4, and most preferably 1:6 to 1:5. It has been found that a higher sieve content, lower matrix content, increases the molecular sieve catalyst composition performance, however, lower sieve content, higher matrix material, improves the attrition resistance of the composition.

[0065] In another embodiment, the formulated molecular sieve catalyst composition contains from about 1% to about 99%, more preferably from about 5% to about 90%, and most preferably from about 10% to about 80%, by weight of the molecular sieve based on the total weight of the molecular sieve catalyst composition.

[0066] In another embodiment, the weight percent of binder in or on the spray dried molecular sieve catalyst composition based on the total weight of the binder, molecular sieve, and matrix material is from about 2% by weight to about 30% by weight, preferably from about 5% by weight to about 20% by weight, and more preferably from about 7% by weight to about 15% by weight.

[0067] Once the molecular sieve catalyst composition is formed in a substantially dry or dried state, to further harden and/or activate the formed catalyst composition, a heat treatment such as calcination, at an elevated temperature is usually performed. A conventional calcination environment is air that typically includes a small amount of water vapor. Typical calcination temperatures are in the range from about 400°C to about 1,000°C, preferably from about 500°C to about 800°C, and most preferably from about 550°C to about 700°C, preferably in a calcination environment such as air, nitrogen, helium, flue gas (combustion product lean in oxygen), or any combination thereof.

[0068] The process for converting a feedstock, especially a feedstock containing one or more oxygenates, in the presence of a molecular sieve catalyst composition of the invention, is carried out in a reaction process in a reactor, where the process is a fixed bed process, a fluidized bed process (includes a turbulent bed process), preferably a continuous fluidized bed process, and most preferably a continuous high velocity fluidized bed process.

[0069] The reaction processes can take place in a variety of catalytic reactors such as hybrid reactors that have a dense bed or fixed bed reaction zones and/or fast fluidized bed reaction zones coupled together, circulating fluidized bed reactors, riser reactors, and the like. Suitable conventional reactor types are described in for example U.S. Patent No. 4,076,796, U.S. Patent No. 6,287,522 (dual riser), and *Fluidization Engineering*, D. Kunii and O. Levenspiel, Robert E. Krieger Publishing Company, New York, New York 1977, which are all herein fully incorporated by reference.

[0070] The preferred reactor type are riser reactors generally described in *Riser Reactor, Fluidization and Fluid-Particle Systems*, pages 48 to 59, F.A. Zenz and D.F. Othmo, Reinhold Publishing Corporation, New York, 1960, and U.S. Patent No. 6,166,282 (fast-fluidized bed reactor), and U.S. Patent Application Serial No. 09/564,613 filed May 4, 2000 (multiple riser reactor), which are all herein fully incorporated by reference.

[0071] In the preferred embodiment, a fluidized bed process or high velocity fluidized bed process includes a reactor system, a regeneration system and a recovery system. The reactor system preferably is a fluid bed reactor system having a first reaction zone within one or more riser reactor(s) and a second reaction zone within at least one disengaging vessel, preferably comprising one or more cyclones. In one embodiment, the one or more riser reactor(s) and disengaging vessel is contained within a single reactor vessel. Fresh feedstock, preferably containing one or more oxygenates, optionally with one or more diluent(s), is fed to the one or more riser reactor(s) in which a zeolite or zeolite-type molecular sieve catalyst composition or coked version thereof is introduced. In one embodiment, the molecular sieve catalyst composition or coked version

thereof is contacted with a liquid or gas, or combination thereof, prior to being introduced to the riser reactor(s), preferably the liquid is water or methanol, and the gas is an inert gas such as nitrogen.

[0072] In an embodiment, the amount of fresh feedstock fed separately or jointly with a vapor feedstock, to a reactor system is in the range of from 0.1 weight percent to about 85 weight percent, preferably from about 1 weight percent to about 75 weight percent, more preferably from about 5 weight percent to about 65 weight percent based on the total weight of the feedstock including any diluent contained therein. The liquid and vapor feedstocks are preferably the same composition, or contain varying proportions of the same or different feedstock with the same or different diluent.

[0073] The feedstock entering the reactor system is preferably converted, partially or fully, in the first reactor zone into a gaseous effluent that enters the disengaging vessel along with a coked molecular sieve catalyst composition. In the preferred embodiment, cyclone(s) within the disengaging vessel are designed to separate the molecular sieve catalyst composition, preferably a coked molecular sieve catalyst composition, from the gaseous effluent containing one or more olefin(s) within the disengaging zone. Cyclones are preferred, however, gravity effects within the disengaging vessel will also separate the catalyst compositions from the gaseous effluent. Other methods for separating the catalyst compositions from the gaseous effluent include the use of plates, caps, elbows, and the like.

[0074] In one embodiment of the disengaging system, the disengaging system includes a disengaging vessel, typically a lower portion of the disengaging vessel is a stripping zone. In the stripping zone the coked molecular sieve catalyst composition is contacted with a gas, preferably one or a combination of steam, methane, carbon dioxide, carbon monoxide, hydrogen, or an inert gas such as argon, preferably steam, to recover adsorbed hydrocarbons from the coked molecular sieve catalyst composition that is then introduced to the regeneration system. In another embodiment, the stripping zone is in a separate vessel from the disengaging vessel and the gas is passed at a gas hourly superficial velocity (GHSV) of from 1 hr<sup>-1</sup> to about 20,000 hr<sup>-1</sup> based on the volume of gas to volume

of coked molecular sieve catalyst composition, preferably at an elevated temperature from 250°C to about 750°C, preferably from about 350°C to 650°C, over the coked molecular sieve catalyst composition.

[0075] The conversion temperature employed in the conversion process, specifically within the reactor system, is in the range of from about 200°C to about 1,000°C, preferably from about 250°C to about 800°C, more preferably from about 250°C to about 750 °C, yet more preferably from about 300°C to about 650°C, yet even more preferably from about 350°C to about 600°C most preferably from about 350°C to about 550°C.

[0076] The conversion pressure employed in the conversion process, specifically within the reactor system, is not critical. The conversion pressure is based on the partial pressure of the feedstock exclusive of any diluent therein. Typically the conversion pressure employed in the process is in the range of from about 0.1 kPaa to about 5 MPaa, preferably from about 5 kPaa to about 1 MPaa , and most preferably from about 20 kPaa to about 500 kPaa.

[0077] The weight hourly space velocity (WHSV), particularly in a process for converting a feedstock containing one or more oxygenates in the presence of a molecular sieve catalyst composition within a reaction zone, is defined as the total weight of the feedstock excluding any diluents to the reaction zone per hour per weight of molecular sieve in the molecular sieve catalyst composition in the reaction zone. The WHSV is maintained at a level sufficient to keep the catalyst composition in a fluidized state within a reactor.

[0078] Typically, the WHSV ranges from about 1 hr<sup>-1</sup> to about 5000 hr<sup>-1</sup>, preferably from about 2 hr<sup>-1</sup> to about 3000 hr<sup>-1</sup>, more preferably from about 5 hr<sup>-1</sup> to about 1500 hr<sup>-1</sup>, and most preferably from about 10 hr<sup>-1</sup> to about 1000 hr<sup>-1</sup>. In one preferred embodiment, the WHSV is greater than 20 hr<sup>-1</sup>, preferably the WHSV for conversion of a feedstock containing methanol and dimethyl ether is in the range of from about 20 hr<sup>-1</sup> to about 300 hr<sup>-1</sup>.

[0079] The superficial gas velocity (SGV) of the feedstock including diluent and reaction products within the reactor system is preferably sufficient to fluidize the molecular sieve catalyst composition within a reaction zone in the reactor.

The SGV in the process, particularly within the reactor system, more particularly within the riser reactor(s), is at least 0.1 meter per second (m/sec), preferably greater than 0.5 m/sec, more preferably greater than 1 m/sec, even more preferably greater than 2 m/sec, yet even more preferably greater than 3 m/sec, and most preferably greater than 4 m/sec. See for example U.S. Patent Application Serial No. 09/708,753 filed November 8, 2000, which is herein incorporated by reference.

**[0080]** In one preferred embodiment of the process for converting an oxygenate to olefin(s) using a silicoaluminophosphate molecular sieve catalyst composition, the process is operated at a WHSV of at least 20 hr<sup>-1</sup> and a Temperature Corrected Normalized Methane Selectivity (TCNMS) of less than 0.016, preferably less than or equal to 0.01. See for example U.S. Patent No. 5,952,538, which is herein fully incorporated by reference.

**[0081]** In another embodiment of the processes for converting an oxygenate such as methanol to one or more olefin(s) using a molecular sieve catalyst composition, the WHSV is from 0.01 hr<sup>-1</sup> to about 100 hr<sup>-1</sup>, at a temperature of from about 350°C to 550°C, and silica to Me<sub>2</sub>O<sub>3</sub> (Me is a Group IIIA or VIII element from the Periodic Table of Elements) molar ratio of from 300 to 2500. See for example EP-0 642 485 B1, which is herein fully incorporated by reference.

**[0082]** Other processes for converting an oxygenate such as methanol to one or more olefin(s) using a molecular sieve catalyst composition are described in PCT WO 01/23500 published April 5, 2001 (propane reduction at an average catalyst feedstock exposure of at least 1.0); which is herein incorporated by reference.

**[0083]** According to one embodiment, the conversion of the primary oxygenate, e.g., methanol, is from 90 wt % to 98 wt %. According to another embodiment the conversion of methanol is from 92 wt % to 98 wt %, preferably from 94 wt % to 98 wt %.

**[0084]** According to another embodiment, the conversion of methanol is above 98 wt % to less than 100 wt %. According to another embodiment, the

conversion of methanol is from 98.1 wt % to less than 100 wt %; preferably from 98.2 wt % to 99.8 wt %. According to another embodiment, the conversion of methanol is from 98.2 wt % to less than 99.5 wt %; preferably from 98.2 wt % to 99 wt %.

**[0085]** The oxygenate to olefin process forms a substantial amount of water as a by-product. Much of this water can be removed by cooling the olefin stream from the oxygenate reactor to a temperature below the condensation temperature of the water in the stream. Preferably, the temperature of the product stream is cooled to a temperature below the condensation temperature of the oxygenate feed for the oxygenate to olefins process. In certain embodiments, it is desirable to cool the product stream below the condensation temperature of methanol.

**[0086]** A quench column is one type of equipment that is effective in cooling the olefin stream from the oxygenate to olefin reaction process. In a quench column, a quenching fluid is directly contacted with the olefin stream to cool the stream to the desired condensation temperature. Condensation produces a condensed water containing stream, which generally exits the quench column as a bottoms stream. Olefin generally exits the column as an overhead stream. It is this overhead stream that contains dimethyl ether which must be separated according to this invention. If a high concentration of water still remains in the overhead, then absorbents can be used as described above to lower the water concentration further.

**[0087]** In one particular embodiment of the invention, the quenched olefin stream is further processed by compression, preferably multi-staged compression. Two, three, four or more stages can be used, with two or three stages being preferred.

**[0088]** During or after multi-stage compression, the olefin stream can be washed using a water absorbent, as described above, if desired. This wash using water absorbent can mitigate problems related to gas hydration and/or separate water phase formation. Preferably, multi-stage compression using a water absorbent wash between stages is preferred. The dimethyl ether and  $C_4^+$  hydrocarbon components are then separated from the olefin stream.



[0089] In one embodiment of this invention, the olefin stream is separated into a first fraction and a second fraction, with a majority of ethylene and/or propylene being separated in the first fraction and a majority of the dimethyl ether being separated in the second fraction. Desirably, separation is carried out at a pressure of less than 200 psig (1,480 kPa absolute). Preferably, separation is carried out at a pressure of from about 100 psig (791 kPa absolute) to about 200 psig (1,480 kPa absolute), more preferably from about 120 psig (929 kPa absolute) to about 180 psig (1,342 kPa absolute).

[0090] In another embodiment of the invention, the separation process is performed in a distillation column such that the first or overhead stream is at a temperature of not greater than about 30°F (-1.1°C). Preferably the first or overhead stream is at a temperature of about 0°F (-17.8°C) to about 30°F (-1.1°C), more preferably about 10°F (-12.2°C) to about 25°F (-3.9°C).

[0091] It is desirable in this invention that the second or bottoms fraction of the distillation column be maintained at a temperature level to reduce fouling problems. In one embodiment, the second fraction is at an average temperature of not greater than about 210°F (99°C), preferably not greater than about 200°F (93°C), and more preferably not greater than about 190°F (88°C).

[0092] It is further desirable in this invention that water absorbent, as described above, be added to the vessel in which the separation of the oxygenated contaminants from the provided olefin stream is performed. The addition of water absorbent directly to the separation vessel can be of additional beneficial in reducing free water and/or clathrate formation in the vessel.

[0093] In one embodiment of the invention, water absorbent is added to the oxygenate separation vessel in an amount sufficient to substantially reduce oxygenate content (e.g., dimethyl ether) or clathrate formation. It is preferred that water absorbent be added to the vessel at a molar ratio of water absorbent to total olefin feed entering the separation vessel of about 4:1 to about 1:5,000. Higher molar ratios of water absorbent to total olefin feed are desirable for reducing oxygenate content; preferably from about 4:1 to about 1:1, more preferably from about 3:1 to about 1.2:1, and most preferably from about 2.5:1 to about 1.5:1.

Lower molar ratios of water absorbent to total olefin feed are desirable for reducing clathrate formation; preferably from about 1:1 to about 1:5,000, more preferably from about 1:100 to about 1:4,000, and most preferably from about 1:500 to about 1:3,000.

**[0094]** In one embodiment of this invention, separation is by conventional distillation. Distillation is carried out using a vessel or tower having internal packing or trays that creates a temperature difference from top to bottom of the tower. The upper portion of the tower is the cooler portion, and higher volatile components in the feed exit from the top of the tower.

**[0095]** In this invention it is desirable to obtain high concentrations of ethylene and propylene from an olefin stream containing dimethyl ether. In one embodiment, the dimethyl ether is separated from the ethylene and propylene in the olefin stream. In this embodiment the ethylene and propylene are recovered in a first fraction, and the dimethyl ether is recovered in a second fraction. Typically, the first fraction will be the overhead or side fraction of a distillation column, and the second fraction will be a bottoms fraction or additional side fraction of a distillation column.

**[0096]** In one embodiment of the invention, a majority of the ethylene and propylene in the provided olefin stream will be separated in a first fraction and a majority of the dimethyl ether in the provided olefin stream will be separated in a second fraction. Preferably, the first fraction will contain at least about 75 % of the ethylene and propylene in the provided olefin stream, more preferably at least about 85 %, and most preferably at least about 95 %.

**[0097]** In another embodiment, at least about 75 % of the dimethyl ether in the provided olefin stream will be separated out in the second fraction. Preferably, at least about 85 % of the dimethyl ether in the provided olefin stream will be separated out in the second fraction, more preferably at least about 95 %, and most preferably at least about 99 %.

**[0098]** A majority of the propane in the provided olefin stream can be separated out in either the first or second fraction. If the majority of the propane is contained in the first fraction, then there will be less separation of heavier

products needed in the second fraction. However, there may be slightly increased levels of dimethyl ether in the first fraction when a majority of the propane is in the first fraction. In this embodiment, at least about 60 % of the propane in the provided olefin stream, preferably at least about 70 %, and more preferably at least about 80 % will be in the first fraction, and the first fraction will contain not greater than about 50 wppm, preferably not greater than about 25 wppm, more preferably not greater than about 10 wppm dimethyl ether, and most preferably not greater than about 5 wppm dimethyl ether.

[0099] If a majority of the propane in the provided olefin stream is separated out in the second fraction, then the concentration of dimethyl ether in the first fraction will be significantly lower. In this embodiment, at least about 60 % of the propane in the provided olefin stream, preferably at least about 70 %, and more preferably at least about 80 % will be in the second fraction, and the second fraction will contain not greater than about 25 wppm, preferably not greater than about 15 wppm, more preferably not greater than about 5 wppm ether, and most preferably not greater than about 1 wppm dimethyl ether.

[0100] In another embodiment of the invention, the second fraction will also contain some hydrocarbon compounds having four or more carbons. These compounds are also known as  $C_4+$  components. The amount of  $C_4+$  components in the second fraction can vary, particularly depending upon the amount of propane in the second fraction. For example the second fraction can contain from about 5 wt % to about 90 wt %  $C_4+$  components. Preferably, the second fraction contains from about 25 wt % to about 80 wt %  $C_4+$  components, more preferably from about 35 wt % to about 75 wt %  $C_4+$  components.

[0101] It is of further advantage in this invention to operate the separation vessel at a temperature and pressure to separate out of the provided olefin stream at least a majority (i.e., at least 50%) of any propadiene which might be present. In this embodiment, the propadiene would preferably be separated out in the second fraction along with dimethyl ether. Preferably, at least about 75 %, more preferably at least about 85 %, and most preferably at least about 95 % of the propadiene would be separated out. Separating out any propadiene out in this

manner would necessarily include separating out a substantial portion of any methyl acetylene which may also be present in the provided olefin stream. This is because methyl acetylene has a lower normal boiling point than propadiene and dimethyl ether. Removing propadiene and methyl acetylene from the provided olefin stream would provide a substantial benefit in that the first fraction containing the ethylene and/or propylene would have a very high concentration of mono-olefinic compounds. Such a stream would need little if any hydroprocessing, which might typically be needed to reduce the number of diolefins or alkylene compounds recovered in the first fraction.

**[0102]** This invention is particularly advantageous for treating the ethylene and propylene streams contained in the first fraction to remove entrained acid gases such as CO<sub>2</sub> which may also be present in such fraction. The advantage is that in this invention the separated ethylene and propylene streams will contain relatively few hydrocarbon components that cause fouling problems in such acid gas treatment systems.

**[0103]** Solid or liquid acid gas treatment systems can be used in this invention. In either system, the acid gas is removed from the ethylene and/or propylene stream in the first fraction by contacting the first fraction with an acid gas absorbent or adsorbent. Examples of such absorbents or adsorbents include amines, potassium carbonate, caustic, alumina, molecular sieves, and membranes, particularly membranes formed of polysulfone, polyimide, polyamide, glassy polymer and cellulose acetate. Solutions containing amines and caustic compounds are preferred, with caustic compounds being more preferred.

**[0104]** Aqueous amine solutions which are useful in this invention can contain any amine compound or compounds suitable for acid gas absorption. Examples include alkanolamines, such as triethanolamine (TEA); methyldiethanolamine (MDEA); diethanolamine (DEA); monoethanolamine (MEA); diisopropanolamine (DIPA); and hydroxyaminoethyl ether (DGA). Effective concentrations can range from about 0.5 to about 8 moles of amine per liter of aqueous solution.

[0105] Piperazine and/or monomethylethanolamine (MMEA) can be added to aqueous amine solutions to enhance their absorption capabilities. These additives can be included in the aqueous solution at a concentration of from about 0.04 to about 2 moles per liter of aqueous solution.

[0106] Caustic compounds which can be used in this invention are alkaline compounds which are effective in removing acid gas from an olefin stream. Examples of such alkaline compounds include sodium hydroxide and potassium hydroxide.

[0107] Following acid gas treating, it is desirable to remove additionally entrained material in the treated ethylene and/or propylene using a water wash. Conventional equipment can be used. It is desirable, however, to further remove additional water from the separated ethylene and/or propylene streams.

[0108] In one embodiment of this invention, the ethylene and propylene in the first fraction is water washed, i.e., contacted with a water stream, prior to acid gas treating. This contacting is particularly advantageous when water absorbent is added to the oxygenate separation vessel, as water absorbent may carry over into the first or overhead fraction. Water washing would then be conducted to remove a substantial portion of water absorbent carry over prior to acid gas treating.

[0109] This invention further includes an optional drying embodiment. In this embodiment, a solid or liquid drying system can be used to remove water and/or additional oxygenated hydrocarbon from the first fraction.

[0110] In the solid drying system, the ethylene and/or propylene having been separated in a first fraction, and optionally acid gas treated and water washed, is contacted with a solid adsorbent to further remove water and oxygenated hydrocarbon to very low levels. Typically, the adsorption process is carried out in one or more fixed beds containing a suitable solid adsorbent.

[0111] Adsorption is useful for removing water and oxygenated hydrocarbons to very low concentrations, and for removing oxygenated hydrocarbons that may not normally be removed by using other treatment systems. Preferably, an adsorbent system used as part of this invention has multiple adsorbent beds. Multiple beds allow for continuous separation without

the need for shutting down the process to regenerate the solid adsorbent. For example, in a three bed system typically one bed is on-line, one bed is regenerated off-line, and a third bed is on stand-by.

[0112] The specific adsorbent solid or solids used in the adsorbent beds depends on the types of contaminants being removed. Examples of solid adsorbents for removing water and various polar organic compounds, such as oxygenated hydrocarbons and absorbent liquids, include aluminas, silica, 3A molecular sieves, 4A molecular sieves, and alumino-silicates. Beds containing mixtures of these sieves or multiple beds having different adsorbent solids can be used to remove water, as well as a variety of oxygenated hydrocarbons.

[0113] In this invention, one or more adsorption beds can be arranged in series or parallel. In one example of a series arrangement, a first bed is used to remove the smallest and most polar molecules which are the easiest to remove. Subsequent beds for removing larger less polar oxygenated species are next in series. As a specific example of one type of arrangement, water is first selectively removed using a 3A molecular sieve. This bed is then followed by one or more beds containing one or more less selective adsorbents such as a larger pore molecular sieve e.g. 13X and/or a high surface area active alumina such as Selexorb CD (Alcoa tradename).

[0114] In another embodiment, the first bed is a 3.6A molecular sieve capable of selectively removing both water and methanol. This bed can then be followed by one or more 13X or active alumina beds as described above.

[0115] The adsorbent beds can be operated at ambient temperature or at elevated temperature as required, and with either upward or downward flow. Regeneration of the adsorbent materials can be carried out by conventional methods including treatment with a stream of a dry inert gas such as nitrogen at elevated temperature.

[0116] In the liquid drying system, a water absorbent is used to remove water from the first fraction. The water absorbent can be any liquid effective in removing water from an olefin stream. Preferably, the water absorbent is the same as that previously described.

[0117] Preferably the olefin from the adsorption beds contains less than about 100 wppm water, more preferably less than about 10 wppm, and most preferably less than 1 wppm. Preferably less than about 10 wppm dimethyl ether is present in the stream leaving the adsorption beds, more preferably less than about 5 wppm, and most preferably less than about 1 wppm.

[0118] The ethylene and propylene streams treated and separated according to this invention can be polymerized to form plastic compositions, e.g., polyolefins, particularly polyethylene and polypropylene. Any conventional process for forming polyethylene or polypropylene can be used. Catalytic processes are preferred. Particularly preferred are metallocene, Ziegler/Natta, chromium oxide and acid catalytic systems. See, for example, U.S. Patent Nos. 3,258,455; 3,305,538; 3,364,190; 5,892,079; 4,659,685; 4,076,698; 3,645,992; 4,302,565; and 4,243,691, the catalyst and process descriptions of each being expressly incorporated herein by reference. In general, these methods involve contacting the ethylene or propylene product with a polyolefin-forming catalyst at a pressure and temperature effective to form the polyolefin product.

[0119] In one embodiment of this invention, the ethylene or propylene product is contacted with a metallocene catalyst to form a polyolefin. Desirably, the polyolefin forming process is carried out at a temperature ranging between about 50°C and about 320°C. The reaction can be carried out at low, medium or high pressure, being anywhere within the range of about 1 bar to about 3200 bar. For processes carried out in solution, an inert diluent can be used. In this type of operation, it is desirable that the pressure be at a range of from about 10 bar to about 150 bar, and preferably at a temperature range of from about 120°C to about 250°C. For gas phase processes, it is preferred that the temperature generally be within a range of about 60°C to 120°C, and that the operating pressure be from about 5 bar to about 50 bar.

[0120] In addition to polyolefins, numerous other olefin derivatives may be formed from the ethylene, propylene and C<sub>4</sub>+ olefins, particularly butylene, separated according to this invention. The olefins separated according to this invention can also be used in the manufacture of such compounds as aldehydes,

acids such as  $C_2$ - $C_{13}$  mono carboxylic acids, alcohols such as  $C_2$ - $C_{12}$  mono alcohols, esters made from the  $C_2$ - $C_{12}$  mono carboxylic acids and the  $C_2$ - $C_{12}$  mono alcohols, linear alpha olefins, vinyl acetate, ethylene dichloride and vinyl chloride, ethylbenzene, ethylene oxide, cumene, acrolein, allyl chloride, propylene oxide, acrylic acid, ethylene-propylene rubbers, and acrylonitrile, and trimers and dimers of ethylene and propylene. The  $C_4$ + olefins, butylene in particular, are particularly suited for the manufacture of aldehydes, acids, alcohols, esters made from  $C_5$ - $C_{13}$  mono carboxylic acids and  $C_5$ - $C_{13}$  mono alcohols and linear alpha olefins.

[0121] One example of separating dimethyl ether from an olefin stream is shown in Figure 1. This example demonstrates one way of obtaining an ethylene and propylene stream substantially depleted of dimethyl ether, as well as  $C_4$ + components. The common factor in this invention, however, is that the dimethyl ether and  $C_4$ + components are substantially removed from the ethylene and/or propylene containing stream prior to caustic treatment. This means that both ethylene and propylene can be recovered in a first fraction, with the dimethyl ether and  $C_4$ + components being recovered in a second fraction. Propane which is present in the olefin stream can be recovered in either the first or second stream, depending upon how low a concentration of dimethyl ether in the first fraction is desired. The ethylene and propylene can then both be recovered and further treated, e.g., caustic wash treated or water wash treated, together or separated and treated separately.

[0122] Figure 1 shows one embodiment in which the olefin to be treated is made in an oxygenate to olefin reaction system. In the Figure, methanol is sent through a line 100 to an oxygenate to olefin reactor 102 where the methanol is converted to an olefin stream comprising methane, ethylene, ethane, propylene, propane, dimethyl ether,  $C_4$ + components, water and other hydrocarbon components. The olefin stream is sent through a line 104 to a quench tower 106 where the olefin is cooled and water and other condensable components are condensed.



[0123] The condensed components, which comprise a substantial amount of water, are withdrawn from the quench tower 106 through a bottoms line 108. A portion of the condensed components are recycled through a line 110 back to the top of the quench tower 106. The line 110 contains a cooling unit, e.g., heat exchanger, (not shown) to further cool the condensed components so as to provide a cooling medium to further cool the components in quench tower 106.

[0124] Olefin vapor leaves the top portion of quench tower 106 through a line 112. The olefin vapor is compressed in compressor 114 and the compressed olefin is passed through a line 116 to a water absorption column 118. In this embodiment, methanol is used as the water absorbent, and is fed to the top portion of the water absorption column 118 through a line 120. Methanol and entrained water, as well as some oxygenated hydrocarbon, is separated as a bottoms stream through a line 122. Olefin is recovered through a line 124. Optionally, the olefin is sent to an additional compressor (not shown), then is input to a distillation column 126.

[0125] The distillation column 126 separates ethylene and propylene, as well as lighter boiling point components from the dimethyl ether and heavier boiling point components, including  $C_4$  + components and methanol remaining from the methanol wash. Additional methanol is added to the distillation column 126 through a line 125 to reduce clathrate and/or free water formation in the distillation column. The ethylene and propylene containing stream exits the distillation column 126 through a line 128, and the heavier boiling point components which include the dimethyl ether and  $C_4$  + components exit the distillation column 126 through a line 130.

[0126] Figure 2 shows subsequent treating and drying of the ethylene and propylene containing stream. Ethylene and propylene flow through the line 128 to a caustic wash column 200. A caustic solution is sent through a line 202 to the top portion of the caustic wash column 200 to remove  $CO_2$ , which is also entrained in the ethylene and propylene containing stream. Spent caustic leaves the caustic wash column 200 through a line 204.

[0127] Caustic treated ethylene and propylene exit caustic wash column 200 through a line 206 to a water wash column 208. Water enters the water wash column through a line 210, and water and absorbed components exit the water wash column 208 through a line 212. Water washed ethylene and propylene exit the water wash column 208 through a line 214, passing through a dryer 216. Dry ethylene and propylene exit the dryer 216 through a line 218.

[0128] Having now fully described this invention, it will be appreciated by those skilled in the art that the invention can be performed within a wide range of parameters within what is claimed, without departing from the spirit and scope of the invention.

**CLAIMS:**

What is claimed is:

1. A method of separating dimethyl ether from an olefin stream, comprising:  
providing an olefin stream containing ethylene, ethane, propylene, propane, and dimethyl ether; and  
separating the olefin stream into a first fraction and a second fraction at a pressure of less than 200 psig (1,480 kPa absolute), wherein the first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream.
2. The method of claim 1, wherein the provided olefin stream further contains water in an amount not greater than 15,000 wppm.
3. The method of claim 2, wherein the water is present in an amount of at least 10 wppm.
4. The method of claim 1, wherein the provided olefin stream further contains at least 500 wppm dimethyl ether.
5. The method of claim 1, wherein the pressure is from 740 kPa to 1,480 kPa.
6. The method of claim 5, wherein the pressure is from 929 kPa to about 1,342 kPa.
7. The method of claim 1, wherein the provided olefin stream contains not greater than 50 wt % dimethyl ether.

8. The method of claim 1, wherein the first fraction contains at least a majority of the propane present in the olefin stream.

9. The method of claim 1, wherein the first fraction contains not greater than 100 wppm dimethyl ether.

10. The method of claim 1, wherein the second fraction contains at least a majority of the propane present in the olefin stream.

11. The method of claim 1, wherein the olefin stream is separated into the first fraction and the second fraction in a distillation column.

12. The method of claim 11, wherein water absorbent is added to the distillation column.

13. The method of claim 12, wherein the second fraction has an average temperature of not greater than 210°F.

14. The method of claim 13, wherein the second fraction has an average temperature of not greater than 93°C.

15. The method of claim 14, wherein the second fraction has an average temperature of not greater than 88°C.

16. The method of claim 12, wherein the water absorbent is added to the distillation column at a molar ratio of water absorbent to total olefin stream to be separated of from 4:1 to 1:5,000.

17. The method of claim 1, wherein the provided olefin stream contains from 50 wt % to 95 wt % ethylene and propylene.

18. The method of claim 1, wherein the provided olefin stream contains from 25 wt % to 75 wt % ethylene.
19. The method of claim 1, wherein the provided olefin stream contains from 25 wt % to 75 wt % propylene.
20. The method of claim 1, wherein the provided olefin stream further comprises CO<sub>2</sub>, and the first fraction further contains at least a majority of the CO<sub>2</sub> in the provided olefin stream.
21. The method of claim 20, further comprising acid gas treating the first fraction.
22. The method of claim 1, wherein the provided olefin stream further comprises C<sub>4</sub>+ hydrocarbon components, and the second fraction further contains at least a majority of the C<sub>4</sub>+ hydrocarbon components in the provided olefin stream.
23. The method of claim 1, further comprising separating the ethylene and propylene in the first fraction and polymerizing the ethylene.
24. The method of claim 1, further comprising separating the ethylene and propylene in the first fraction and polymerizing the propylene.
25. The method of claim 12, further comprising contacting the first fraction with water, acid gas treating the water contacted first fraction, and drying the acid gas treated first fraction.
26. A method of separating dimethyl ether from an olefin stream, comprising:

contacting oxygenate with a molecular sieve catalyst to form an olefin stream, wherein the olefin stream contains ethylene, ethane, propylene, propane, and dimethyl ether; and

separating the olefin stream into a first fraction and a second fraction at a pressure of less than 1,480 kPa, wherein the first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream.

27. The method of claim 26, further comprising contacting the olefin stream formed from contacting the oxygenate with the molecular sieve catalyst with water absorbent prior to separating into the first and second fraction.

28. The method of claim 27, wherein the water absorbent is contacted with the olefin stream at a molar ratio of water absorbent to total olefin of 1:2 to 1:200.

29. The method of claim 26, wherein the olefin stream contacted with the water absorbent contains water in an amount not greater than 15,000 wppm.

30. The method of claim 26, wherein the olefin stream contacted with the water absorbent contains at least 500 wppm dimethyl ether.

31. The method of claim 26, wherein the pressure is from 791 kPa to 1480 kPa.

32. The method of claim 31, wherein the pressure is from 929 kPa to about 1,342 kPa.

33. The method of claim 26, wherein the first fraction contains at least a majority of the propane present in the olefin stream.

34. The method of claim 28, wherein the first fraction contains not greater than 100 wppm dimethyl ether.

35. The method of claim 28, wherein the second fraction contains at least a majority of the propane present in the olefin stream.

36. The method of claim 26, wherein the olefin stream is separated into the first fraction and the second fraction in a distillation column.

37. The method of claim 36, wherein the second fraction has an average temperature of not greater than 210°F.

38. The method of claim 37, wherein the second fraction has an average temperature of not greater than 93°C.

39. The method of claim 38, wherein the second fraction has an average temperature of not greater than 88°C.

40. The method of claim 36, wherein water absorbent is added to the distillation column.

41. The method of claim 40, wherein the water absorbent is added to the distillation column at a molar ratio of water absorbent to total olefin stream to be separated of from 4:1 to 1:5,000.

42. The method of claim 26, wherein the provided olefin stream further comprises CO<sub>2</sub>, and the first fraction further contains at least a majority of the CO<sub>2</sub> in the provided olefin stream.

43. The method of claim 42, further comprising acid gas treating the first fraction.

44. The method of claim 26, wherein the provided olefin stream further comprises  $C_4+$  hydrocarbon components, and the second fraction further contains at least a majority of the  $C_4+$  hydrocarbon components in the provided olefin stream.

45. The method of claim 26, further comprising separating the ethylene and propylene in the first fraction and polymerizing the ethylene.

46. The method of claim 26, further comprising separating the ethylene and propylene in the first fraction and polymerizing the propylene.

47. The method of claim 36, further comprising contacting the first fraction with water, acid gas treating the water contacted first fraction, and drying the acid gas treated first fraction.

48. A method of separating dimethyl ether from an olefin stream, comprising:

contacting oxygenate with a molecular sieve catalyst to form an olefin stream, wherein the olefin stream contains ethylene, ethane, propylene, propane, dimethyl ether and water;

removing water from the olefin stream so that the olefin stream contains not greater than 15,000 wppm water; and

separating the olefin stream containing not greater than 15,000 wppm water into a first fraction and a second fraction at a pressure of less than 1,480 kPa, wherein the first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream.



49. The method of claim 48, wherein the water is removed from the olefin stream by contacting the olefin stream with water absorbent at a molar ratio of water absorbent to total olefin of 1:2 to 1:200.

50. The method of claim 48, wherein the olefin stream is separated into the first fraction and the second fraction in a distillation column.

51. The method of claim 50, wherein water absorbent is added to the distillation column.

52. The method of claim 51, wherein the water absorbent is added to the distillation column at a molar ratio of water absorbent to total olefin stream to be separated of from 4:1 to 1:5,000.

53. The method of claim 52, wherein the olefin stream is separated at a pressure of from 791 kPa to 1,480 kPa.

54. The method of claim 48, wherein the provided olefin stream comprises further CO<sub>2</sub>, and the first fraction further contains at least a majority of the CO<sub>2</sub> in the provided olefin stream.

55. The method of claim 54, further comprising acid gas treating the first fraction.

56. The method of claim 48, wherein the provided olefin stream further comprises C<sub>4</sub>+ hydrocarbon components, and the second fraction further contains at least a majority of the C<sub>4</sub>+ hydrocarbon components in the provided olefin stream.

57. The method of claim 48, further comprising separating the ethylene and propylene in the first fraction and polymerizing the ethylene.

58. The method of claim 48, further comprising separating the ethylene and propylene in the first fraction and polymerizing the propylene.

59. The method of claim 50, further comprising contacting the first fraction with water, acid gas treating the water contacted first fraction, and drying the acid gas treated first fraction.

60. A method of separating dimethyl ether from an olefin stream, comprising:

providing an olefin stream containing ethylene, ethane, propylene, propane, and dimethyl ether; and

separating the olefin stream into a first fraction containing at least a majority of the ethylene and propylene present in the olefin stream, and a second fraction containing at least a majority of the dimethyl ether present in the olefin stream, wherein the olefin stream is separated at a pressure of less than 1,480 kPa and such that the second fraction has an average temperature of not greater than 210°F.

61. The method of claim 60, wherein the olefin stream is separated into the first fraction and the second fraction in a distillation column.

62. The method of claim 61, wherein water absorbent is added to the distillation column.

63. The method of claim 62, wherein the water absorbent is added to the distillation column at a molar ratio of water absorbent to total olefin stream to be separated of from 4:1 to 1:5,000.

64. The method of claim 62, wherein the olefin stream is separated at a pressure of from 791 kPa to 1,480 kPa.

65. The method of claim 60, wherein the provided olefin stream further comprises CO<sub>2</sub>, and the first fraction further contains at least a majority of the CO<sub>2</sub> in the provided olefin stream.

66. The method of claim 65, further comprising acid gas treating the first fraction.

67. The method of claim 60, wherein the provided olefin stream further comprises C<sub>4</sub>+ hydrocarbon components, and the second fraction further contains at least a majority of the C<sub>4</sub>+ hydrocarbon components in the provided olefin stream.

68. The method of claim 62, further comprising separating the ethylene and propylene in the first fraction and polymerizing the ethylene.

69. The method of claim 62, further comprising separating the ethylene and propylene in the first fraction and polymerizing the propylene.

70. The method of claim 61, further comprising contacting the first fraction with water, acid gas treating the water contacted first fraction, and drying the acid gas treated first fraction.

71. The method of claim 60, wherein the second fraction has an average temperature of not greater than 93°C

72. The method of claim 71, wherein the second fraction has an average temperature of not greater than 88°C.

73. A method of separating dimethyl ether from an olefin stream, comprising:

providing an olefin stream containing ethylene, ethane, propylene, propane, propadiene and dimethyl ether; and

separating the olefin stream into a first fraction containing at least a majority of the ethylene and propylene present in the olefin stream, and a second fraction containing at least a majority of the dimethyl ether and propadiene present in the olefin stream, wherein the olefin stream is separated at a pressure of less than 1,480 kPa and such that the second fraction has an average temperature of not greater than 210°F.

74. The method of claim 73, wherein the olefin stream is separated into the first fraction and the second fraction in a distillation column.

75. The method of claim 74, wherein water absorbent is added to the distillation column.

76. The method of claim 75, wherein the water absorbent is added to the distillation column at a molar ratio of water absorbent to total olefin stream to be separated of from 4:1 to 1:5,000.

77. The method of claim 75, wherein the olefin stream is separated at a pressure of from 791 kPa to 1,480 kPa.

78. The method of claim 73, wherein the provided olefin stream further comprises CO<sub>2</sub>, and the first fraction further contains at least a majority of the CO<sub>2</sub> in the provided olefin stream.

79. The method of claim 78, further comprising acid gas treating the first fraction.

80. The method of claim 73, wherein the provided olefin stream further comprises C<sub>4</sub>+ hydrocarbon components, and the second fraction further contains

at least a majority of the  $C_4+$  hydrocarbon components in the provided olefin stream.

81. The method of claim 73, further comprising separating the ethylene and propylene in the first fraction and polymerizing the ethylene.

82. The method of claim 73, further comprising separating the ethylene and propylene in the first fraction and polymerizing the propylene.

83. The method of claim 74, further comprising contacting the first fraction with water, acid gas treating the water contacted first fraction, and drying the acid gas treated first fraction.

84. The method of claim 83, wherein the second fraction has an average temperature of not greater than  $93^{\circ}\text{C}$ .

85. The method of claim 84, wherein the second fraction has an average temperature of not greater than  $88^{\circ}\text{C}$ .

86. A method of separating dimethyl ether from an olefin stream, comprising:

providing an olefin stream containing ethylene, ethane, propylene, propane, and dimethyl ether; and

separating the olefin stream into a first fraction and a second fraction in a distillation column, wherein the first fraction contains at least a majority of the ethylene and propylene present in the olefin stream, and the second fraction contains at least a majority of the dimethyl ether present in the olefin stream.

87. The method of claim 86, wherein the olefin stream is separated into the first and second fractions at a pressure of less than 1,480 kPa.

88. The method of claim 86, wherein the second fraction has an average temperature of not greater than 210°F.

89. The method of claim 88, wherein the second fraction has an average temperature of not greater than 93°C.

90. The method of claim 89, wherein the second fraction has an average temperature of not greater than 88°C.

91. The method of claim 86, wherein the provided olefin stream further contains water in an amount not greater than 15,000 wppm.

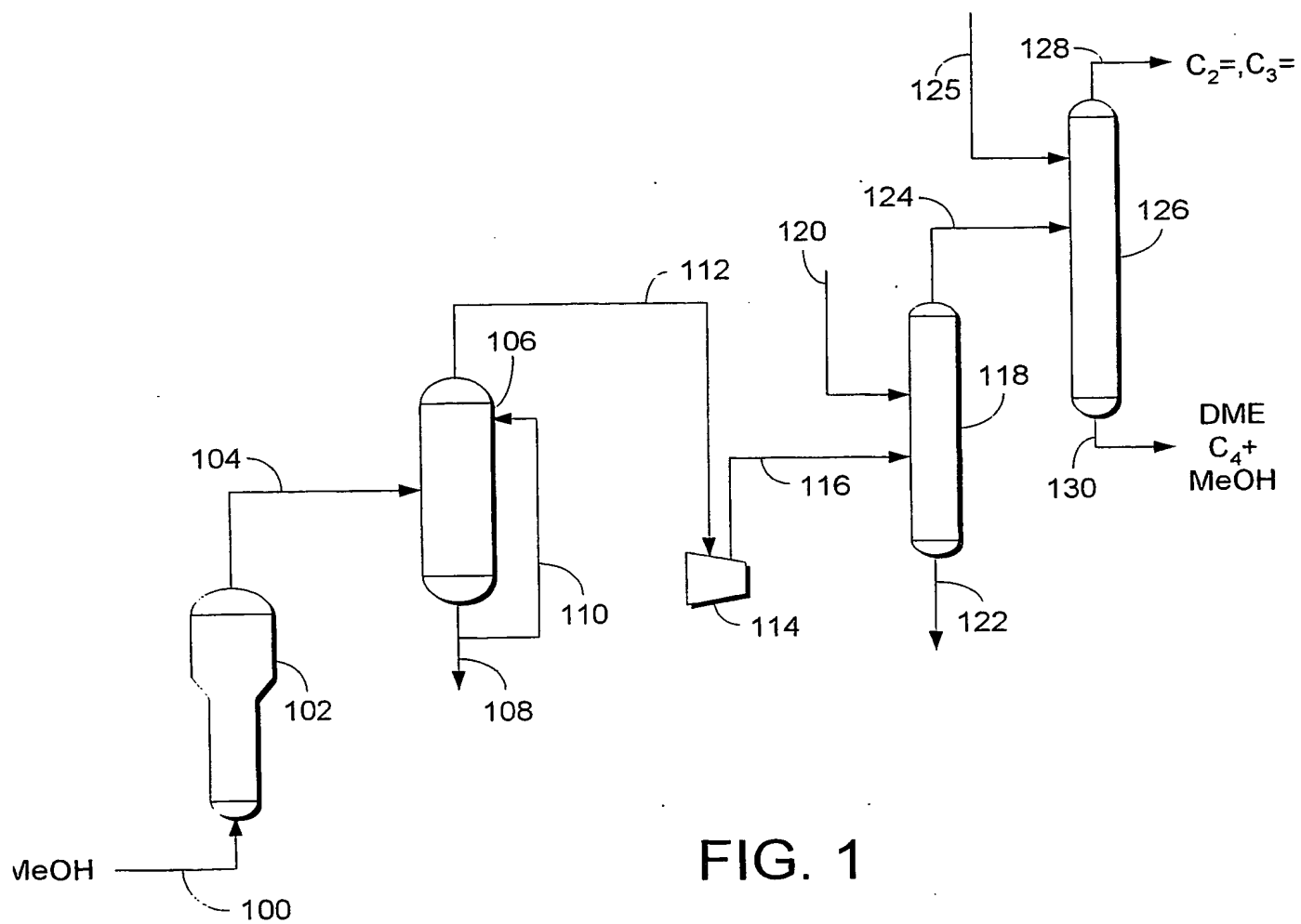
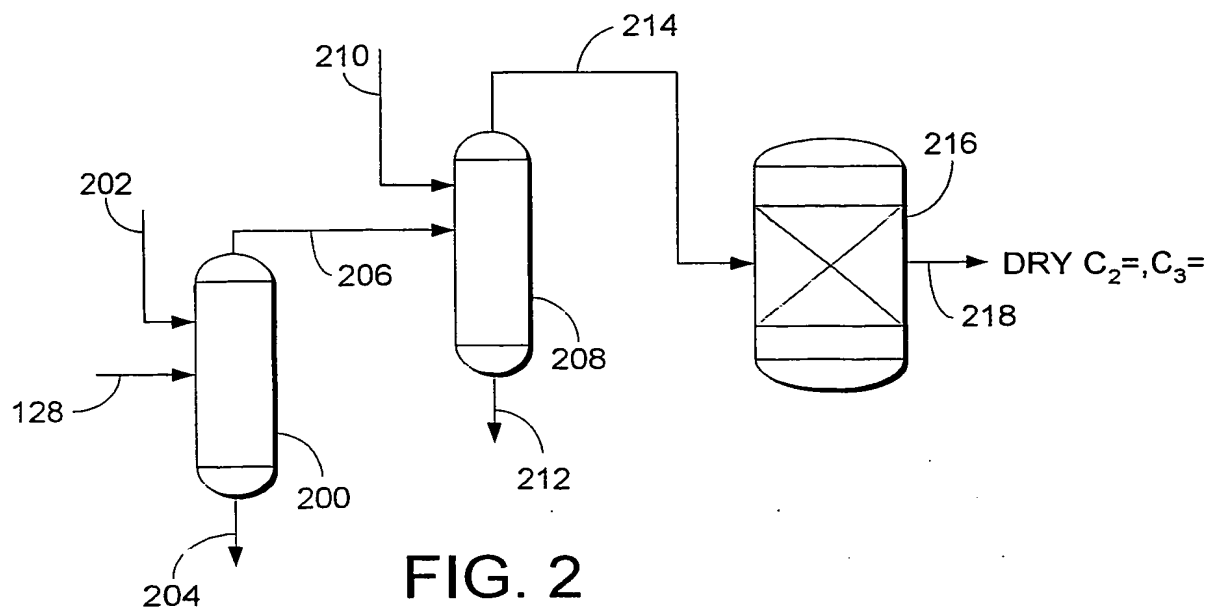


FIG. 1





## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/26119

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C7/04 C07C1/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 474 647 A (ASSELINEAU LIONEL ET AL) 2 October 1984 (1984-10-02) cited in the application ----	
A	US 5 336 841 A (ADAMS JOHN R) 9 August 1994 (1994-08-09) ----	
A	US 5 609 734 A (STREICHER CHRISTIAN ET AL) 11 March 1997 (1997-03-11) -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

7 October 2002

Date of mailing of the international search report

30/10/2002

Name and mailing address of the ISA

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Authorized officer

Van Geyt, J

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-10, 17-24, 26-35, 42-46, 48, 49, 54-58, 60, 73, 78-91  
(all in part),

Present claims 1, 26, 48, 60, 73 and 86 relate to an extremely large number of possible methods. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the separation by distillation:

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/26119

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/26119

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4474647	A	02-10-1984	FR 2504522 A1	29-10-1982
			DE 3214431 A1	11-11-1982
US 5336841	A	09-08-1994	EP 0619286 A1	12-10-1994
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			BR 9404346 A	04-07-1995
			CA 2135127 A1	06-05-1995
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			DE 69401419 T2	24-04-1997
			EP 0652194 A1	10-05-1995
			ES 2099555 T3	16-05-1997
			JP 7206745 A	08-08-1995